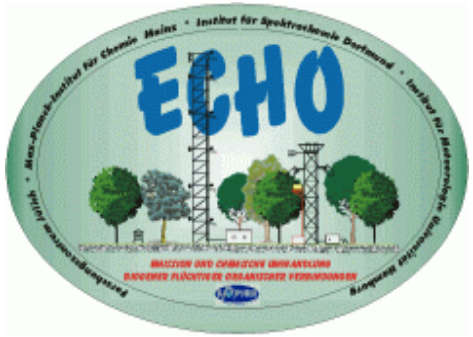


Speciated Analysis of biogenic VOCs during the ECHO-Campaign

Bernhard Mittermaier, Dieter Klemp
Research Center Juelich, Germany

Objectives

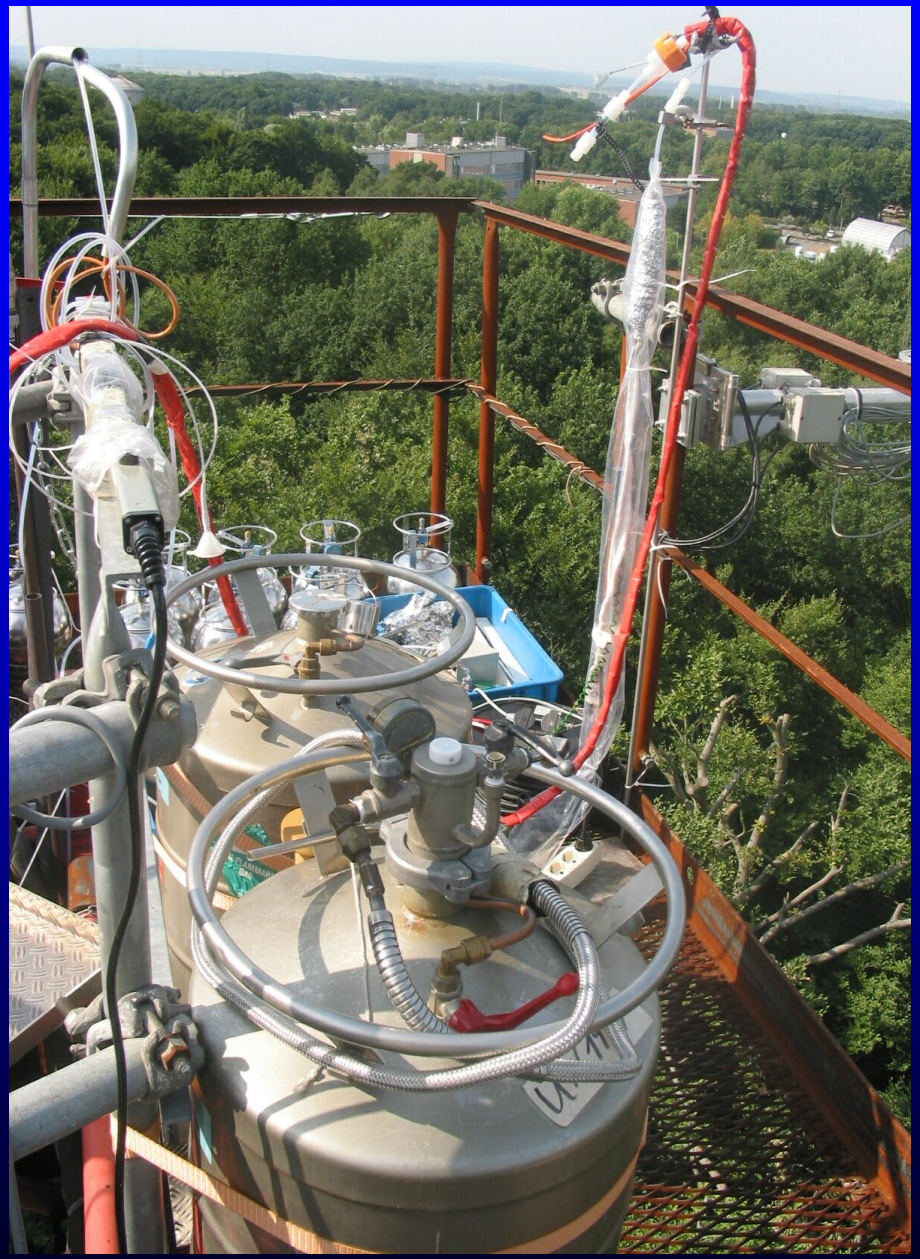
Detection of the complete VOC-pattern during some intensive campaigns at the main tower

- 06.-07.07.03 Ground measurements
- 15.-16.07.03 Vertical profile
- 19.-20.07.03 38m height (above canopy)
- 28.-29.07.03 18m height (in canopy)
- January 2004 anthropogenic background

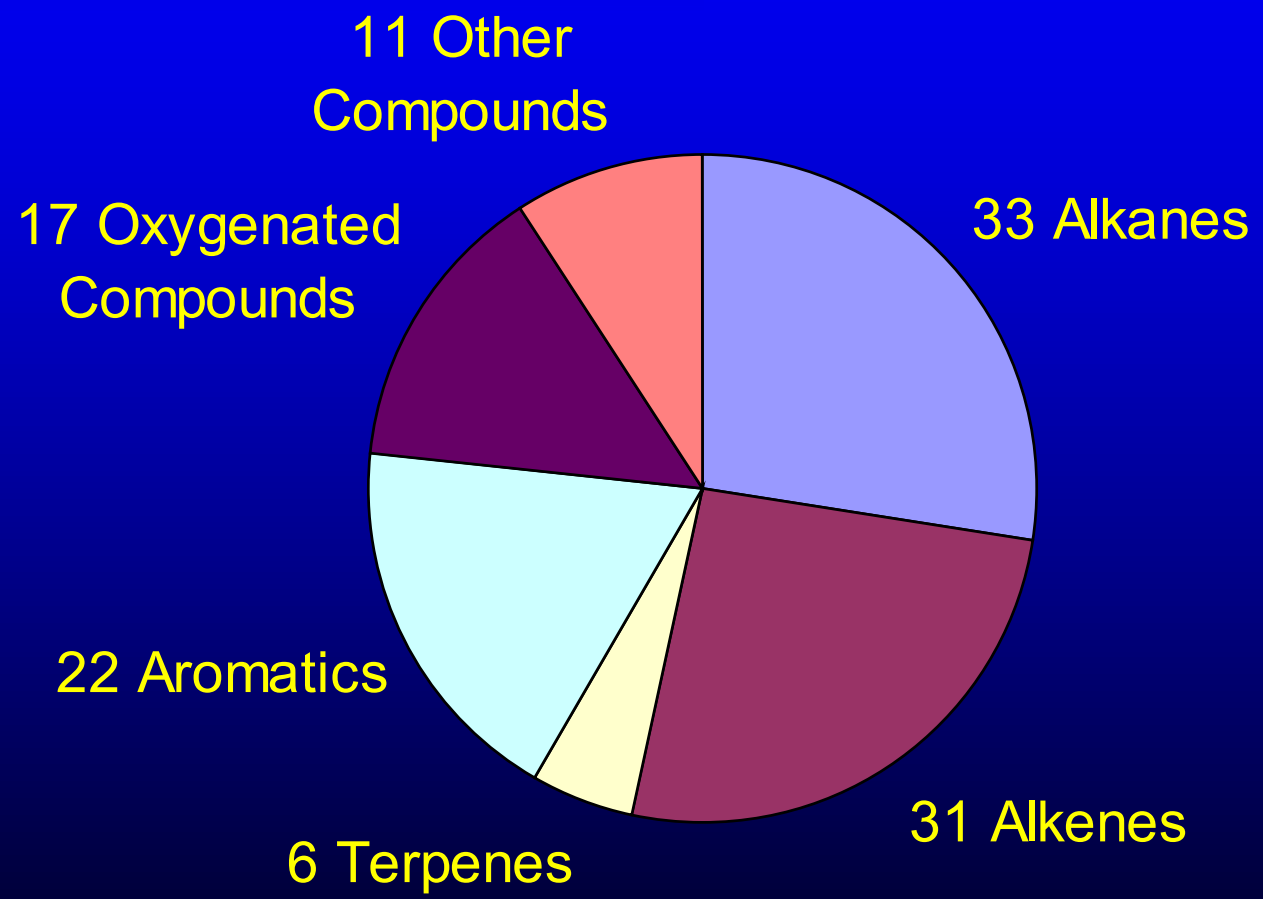
Instrumentation

- passive sampling into evacuated SilcoCan™-canisters
- sampling time: 30 – 60 min
- sampling volume: 3-5 liters
- ozone scrubbing: heated capillary (100°C)
- detection: offline with GC-FID (MSD)


SilcoCan



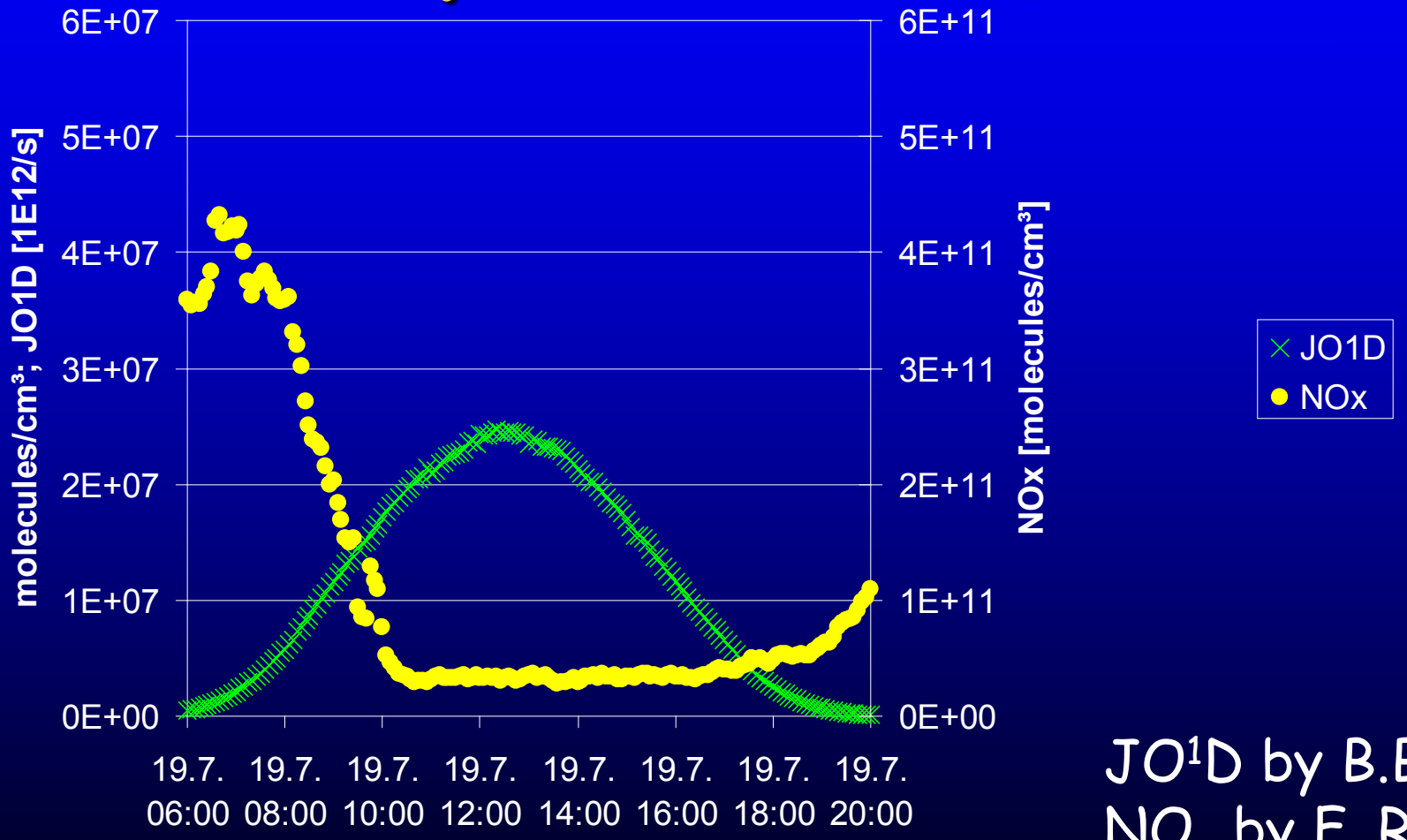
120 Analytes



Average of July 2003

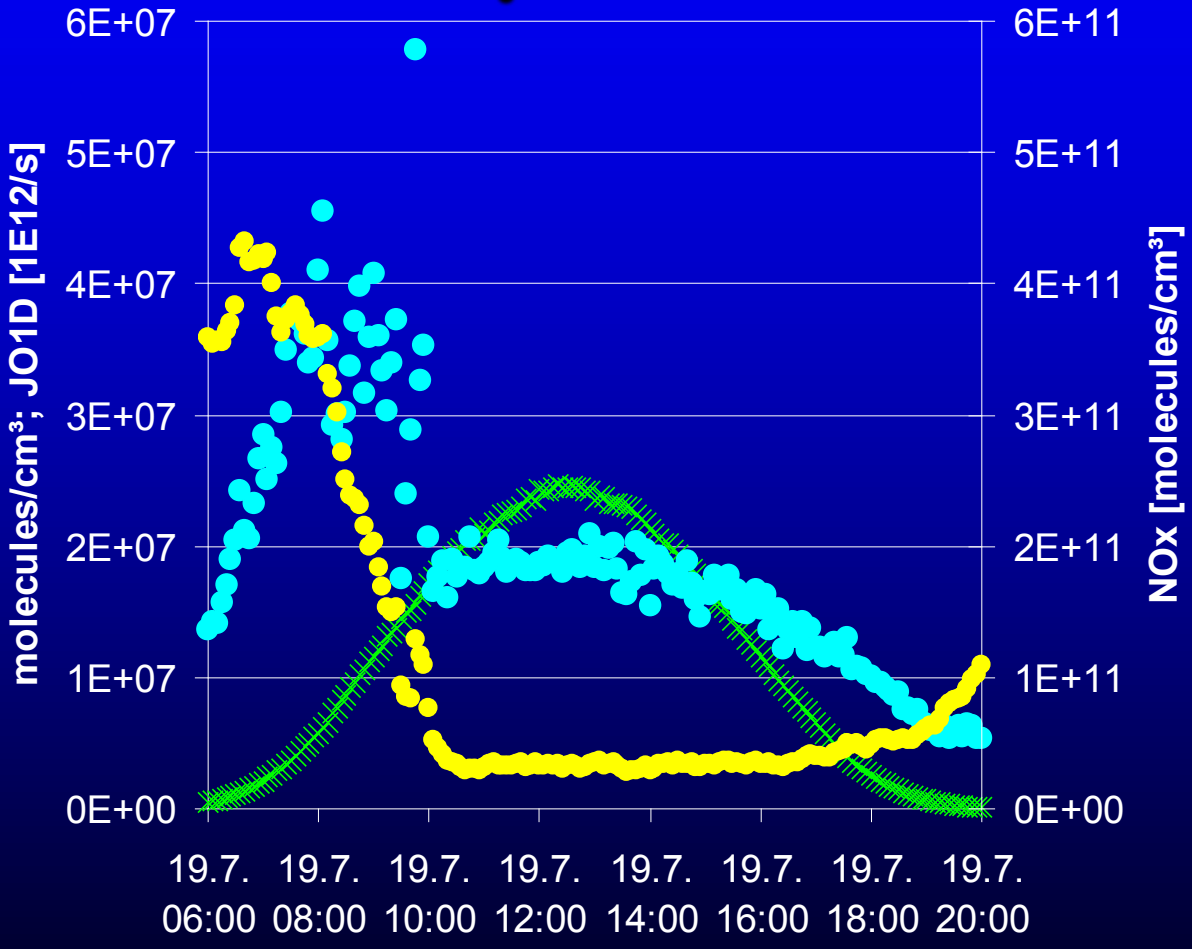
pptV		ppb·**kOH**·10E12		ppb·**kO_3**·10E18		ppb·**kNO_3**·10E15		µg/m^3·**POCP**	
Sum	**25606**	**Sum**	**9,985**	**Sum**	**1,783**	**Sum**	**74,435**	**Sum**	**2716**
Fraction Isopre	11%	Fraction Isopre	70%	Fraction Isopre	54%	Fraction Isopre	65%	Fraction Isopre	32%
Methanole	5094	Isoprene	6,947	Isoprene	0,962	Isoprene	48,270	Isoprene	866
Acetone	4797	Methyl vinyl ket	0,210	cis-2-Butene	0,142	Cyclopentadien	5,260	Acetone	107
Isoprene	2848	Cyclopentadier	0,207	1,3-Pentadiene	0,083	alpha-Pinene	5,039	Methyl vinyl ket	100
Ethane	1982	1-Hexene	0,189	Methylcycloper	0,077	Limonene	4,651	Ethanole	100
Ethanole	1369	1,3-Pentadiene	0,187	1-Butene / i-Bu	0,073	1,3-Pentadiene	2,967	Methanole	87
Propane	791	1-Butene / i-Bu	0,183	alpha-Pinene	0,070	Sabinene	2,332	Toluene	82
Methyl vinyl ke	696	Butyraldehyde	0,149	Limonene	0,069	beta-Pinene	1,698	1-Hexene	72
Ethene	534	Methacrolein	0,127	1-Hexene	0,056	1-Butene / i-Bu	1,212	1-Butene / i-Bu	71
n-Butane	379	Methanole	0,118	Methyl vinyl ket	0,054	1,3-Hexadiene	0,890	o-Ethyltoluene	65
Toluene	343	Ethanole	0,109	2-Methyl-2-bute	0,033	2-Methyl-2-bute	0,788	Butyraldehyde	61

Contribution of isoprene to local ozone production (MCM3)



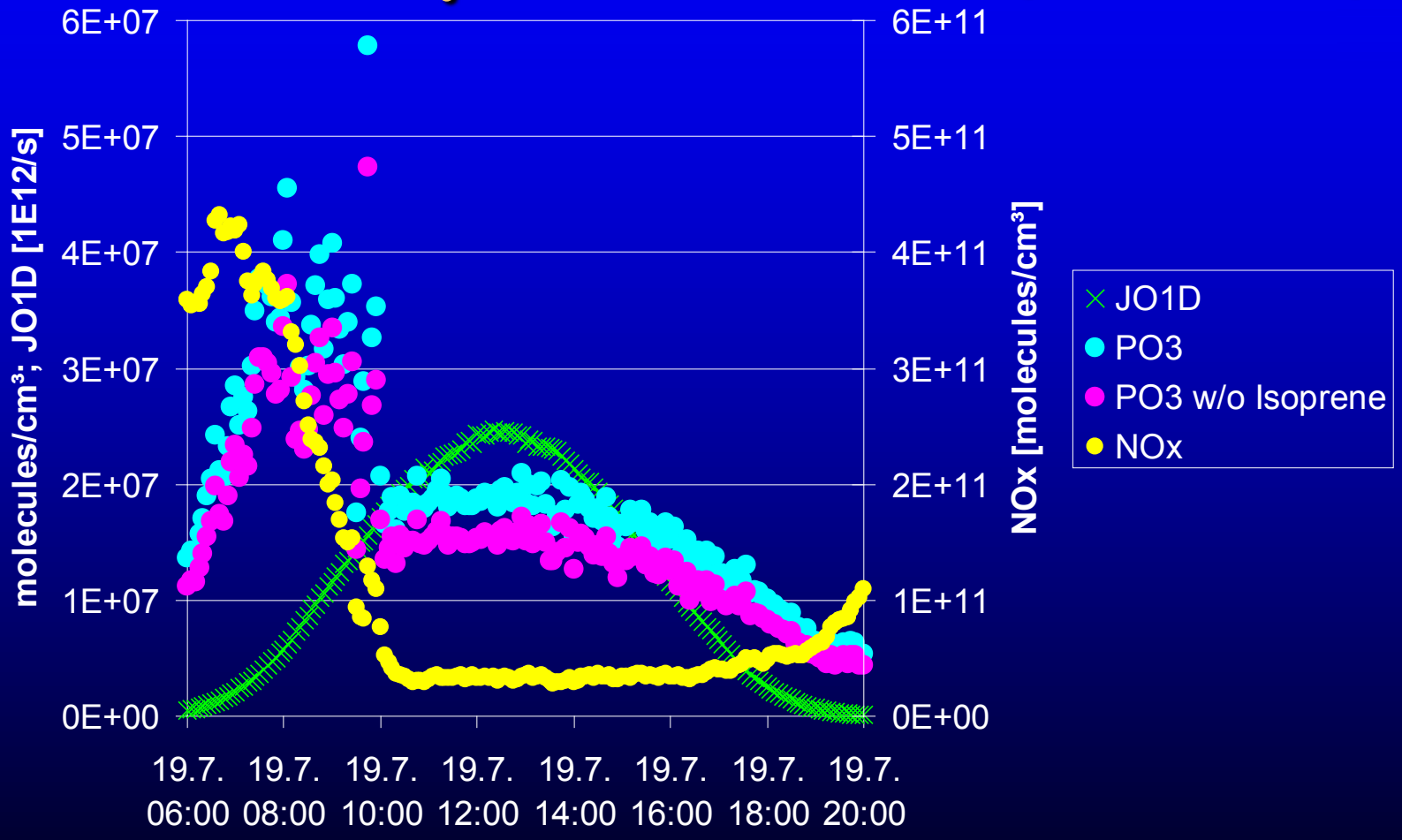
JO^1D by B.Bohn
NO_x by F. Rohrer

Contribution of isoprene to local ozone production (MCM3)

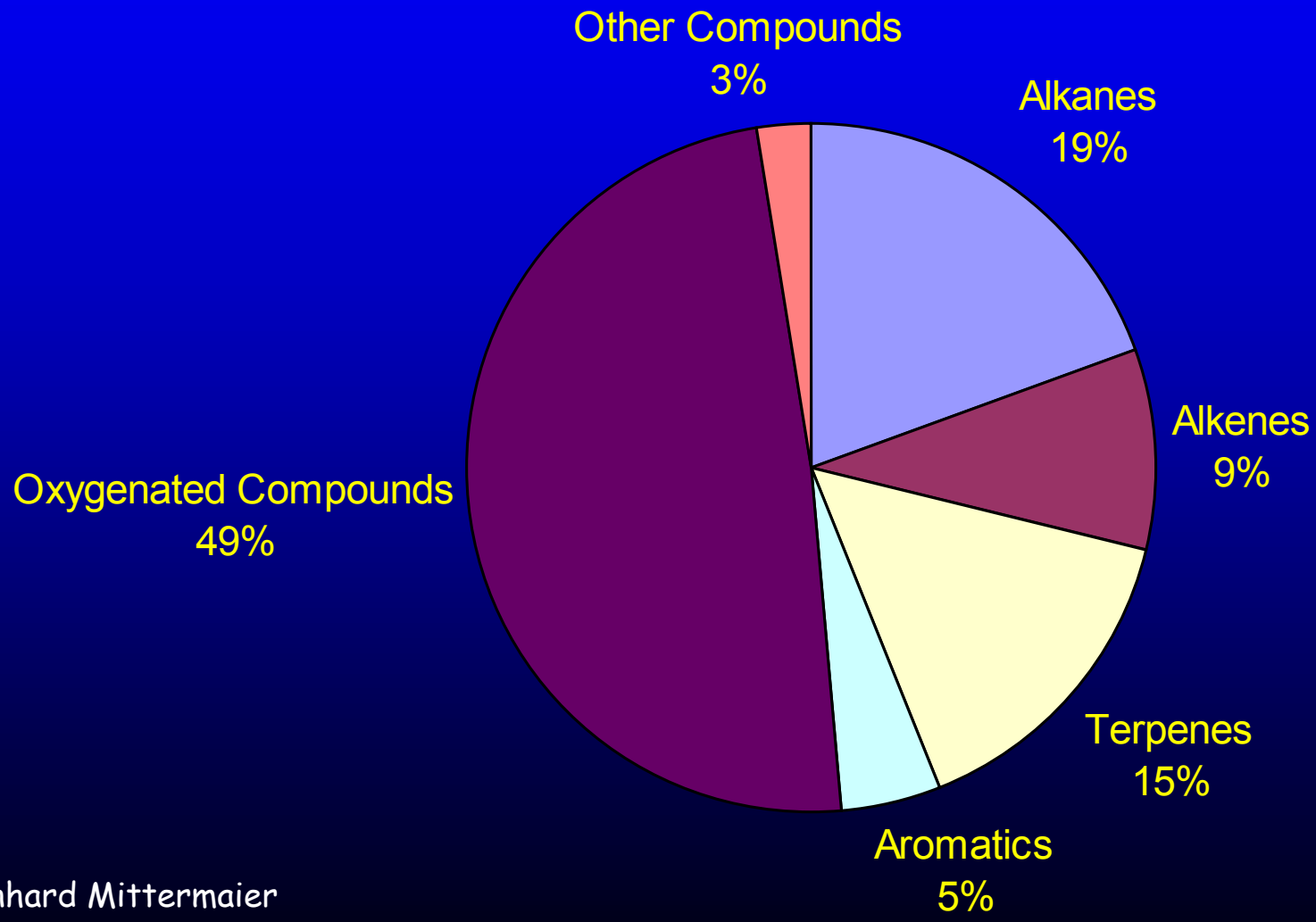


PO3 ~ NO·HO2 + NO·RO2

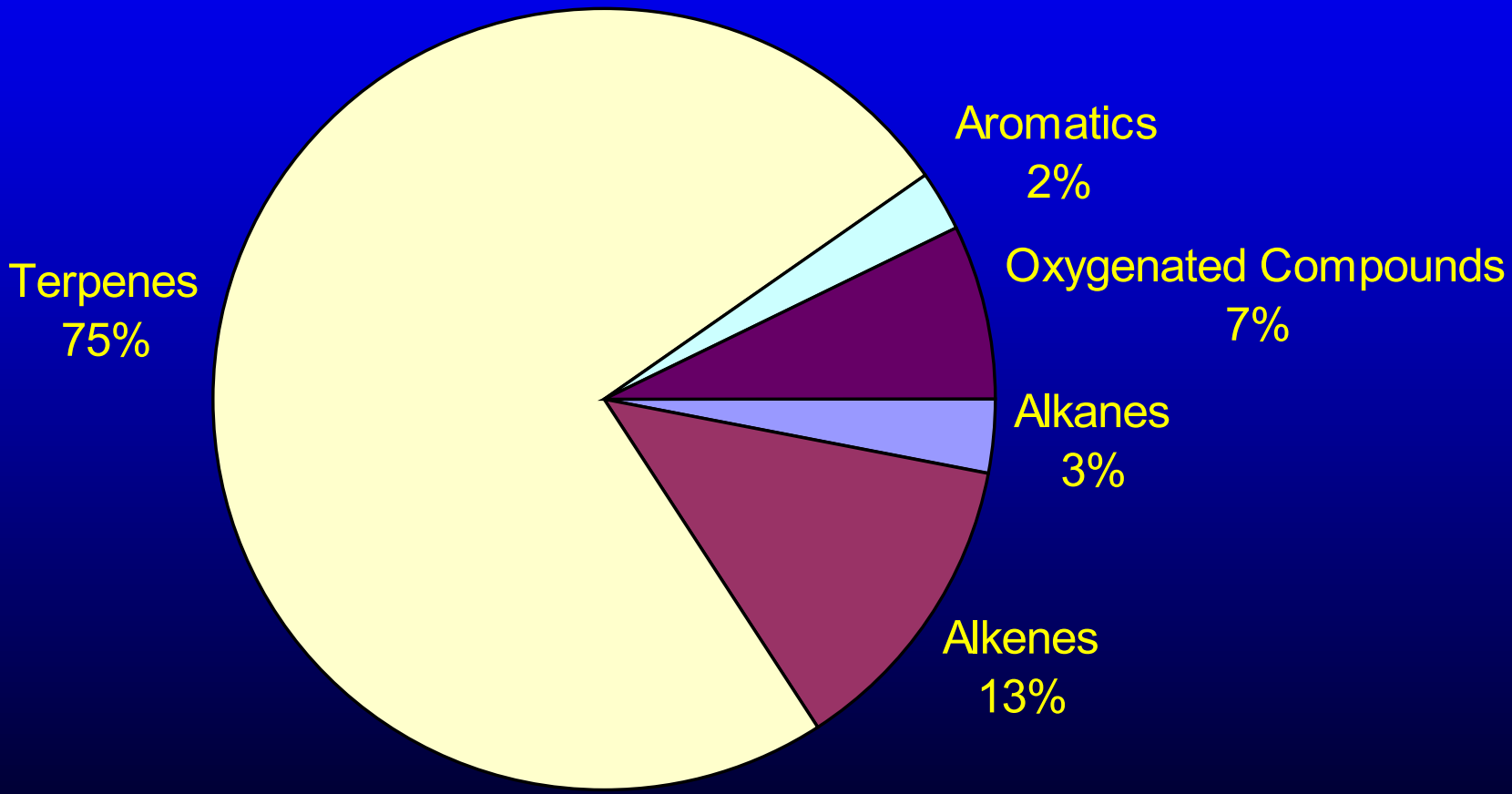
Contribution of isoprene to local ozone production (MCM3)



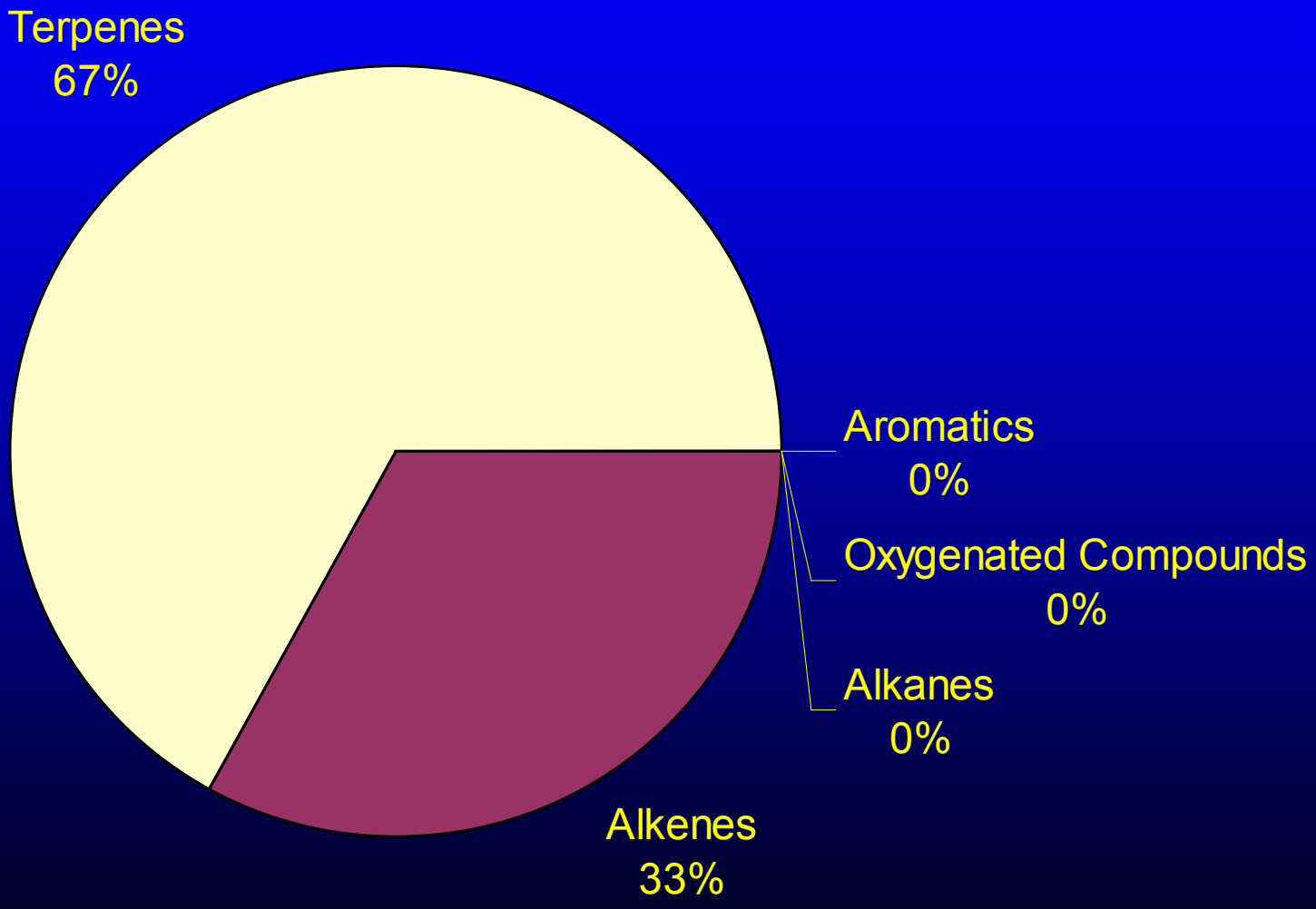
Contributions to mixing ratio



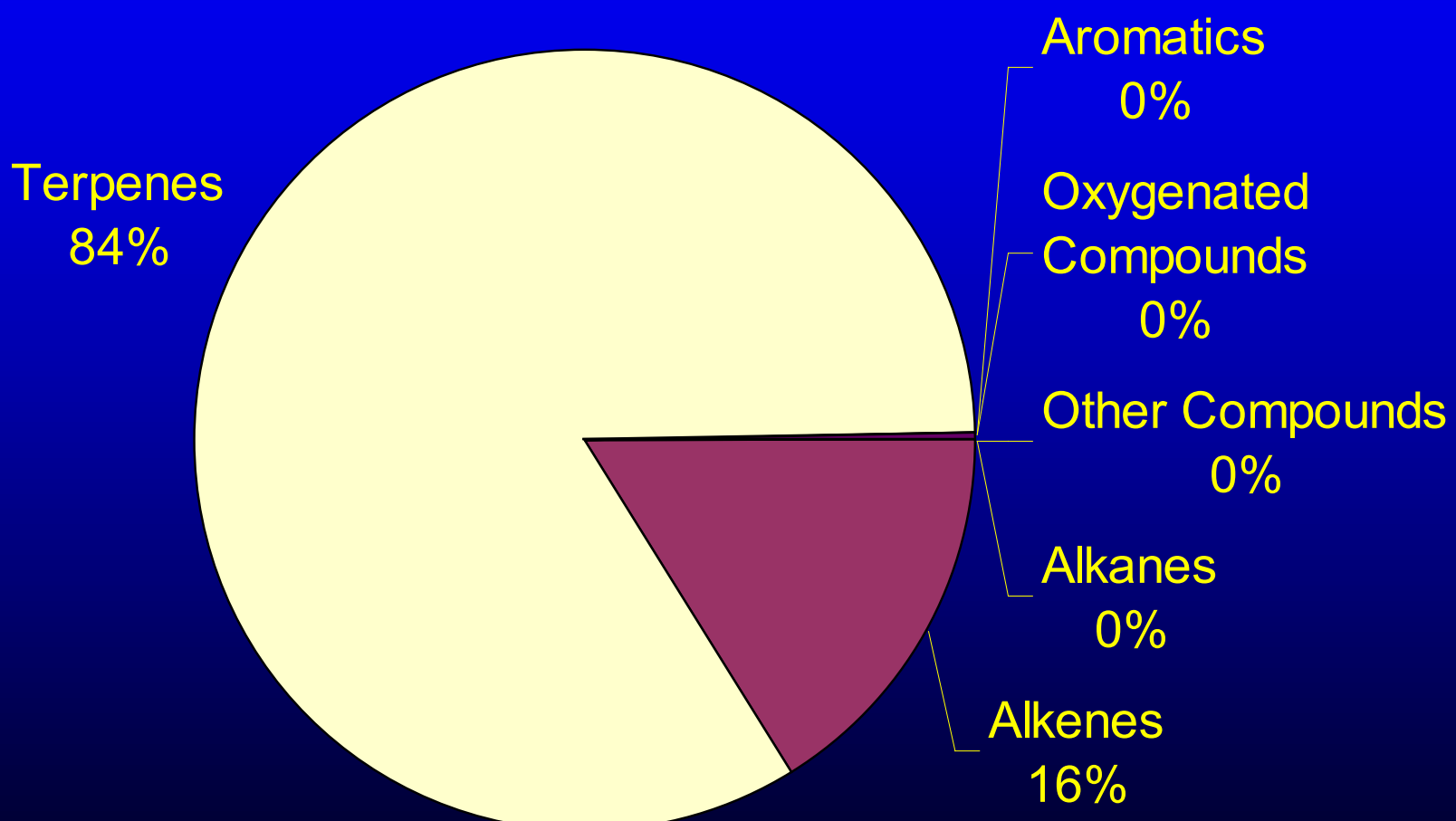
Contributions to OH-Reactivity



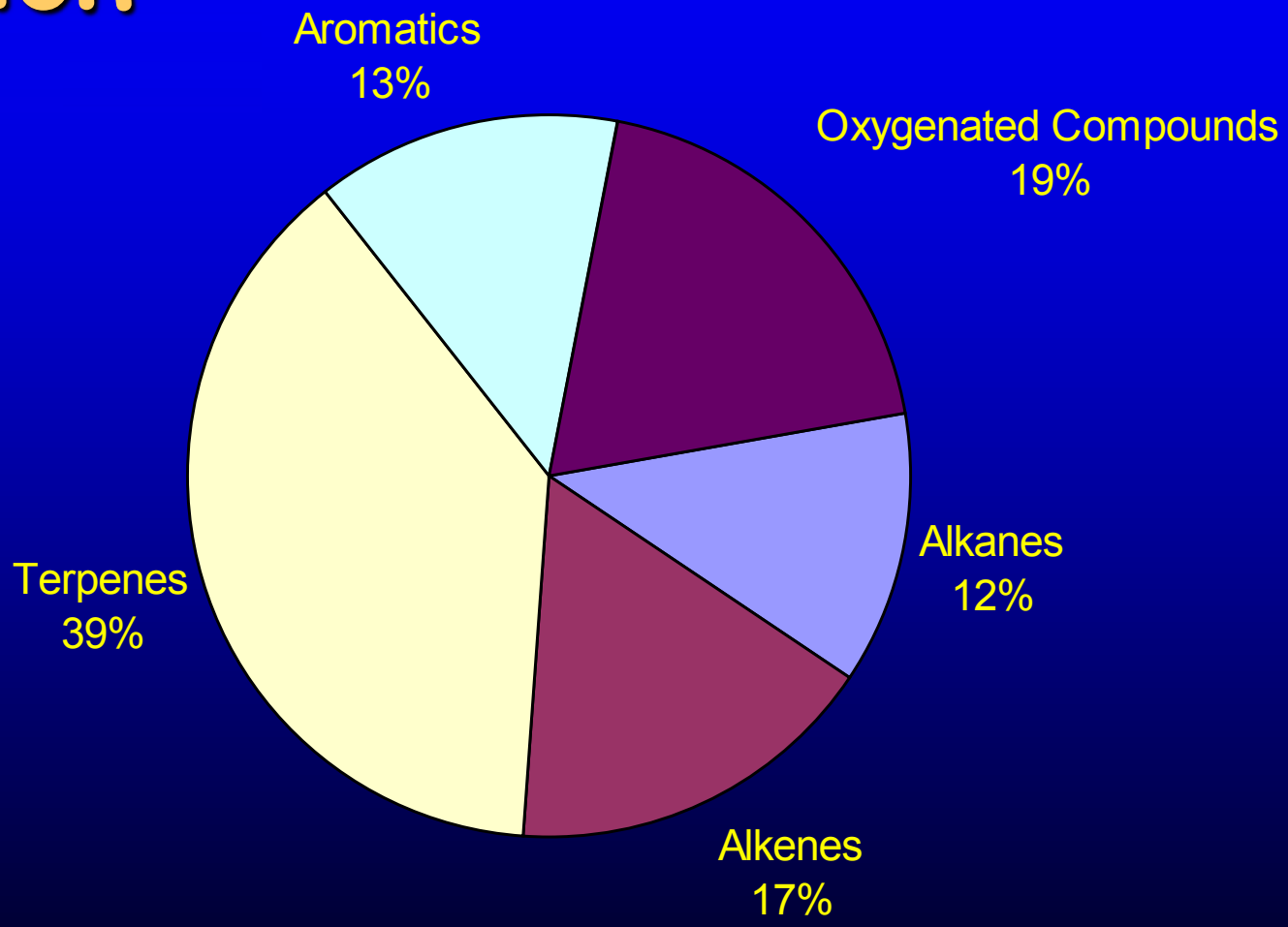
Contributions to O_3-Reactivity



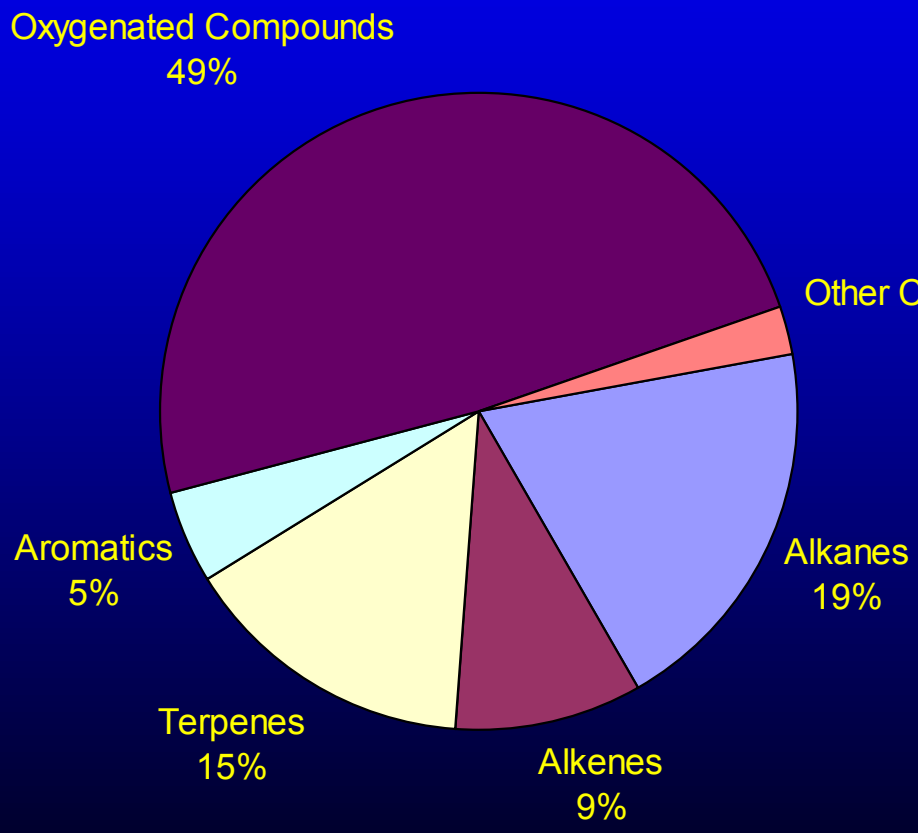
Contributions to NO_3-Reactivity

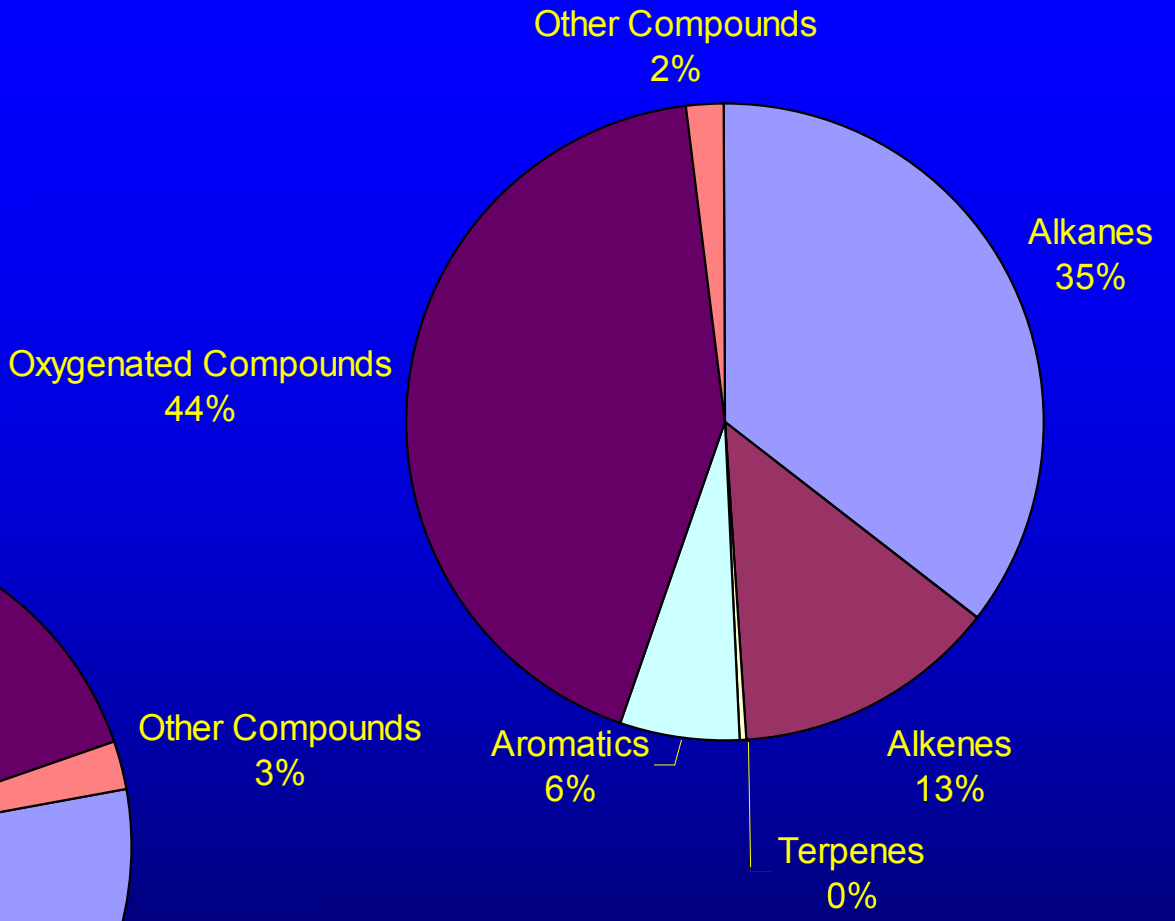


Contributions to local ozone production



July 2003



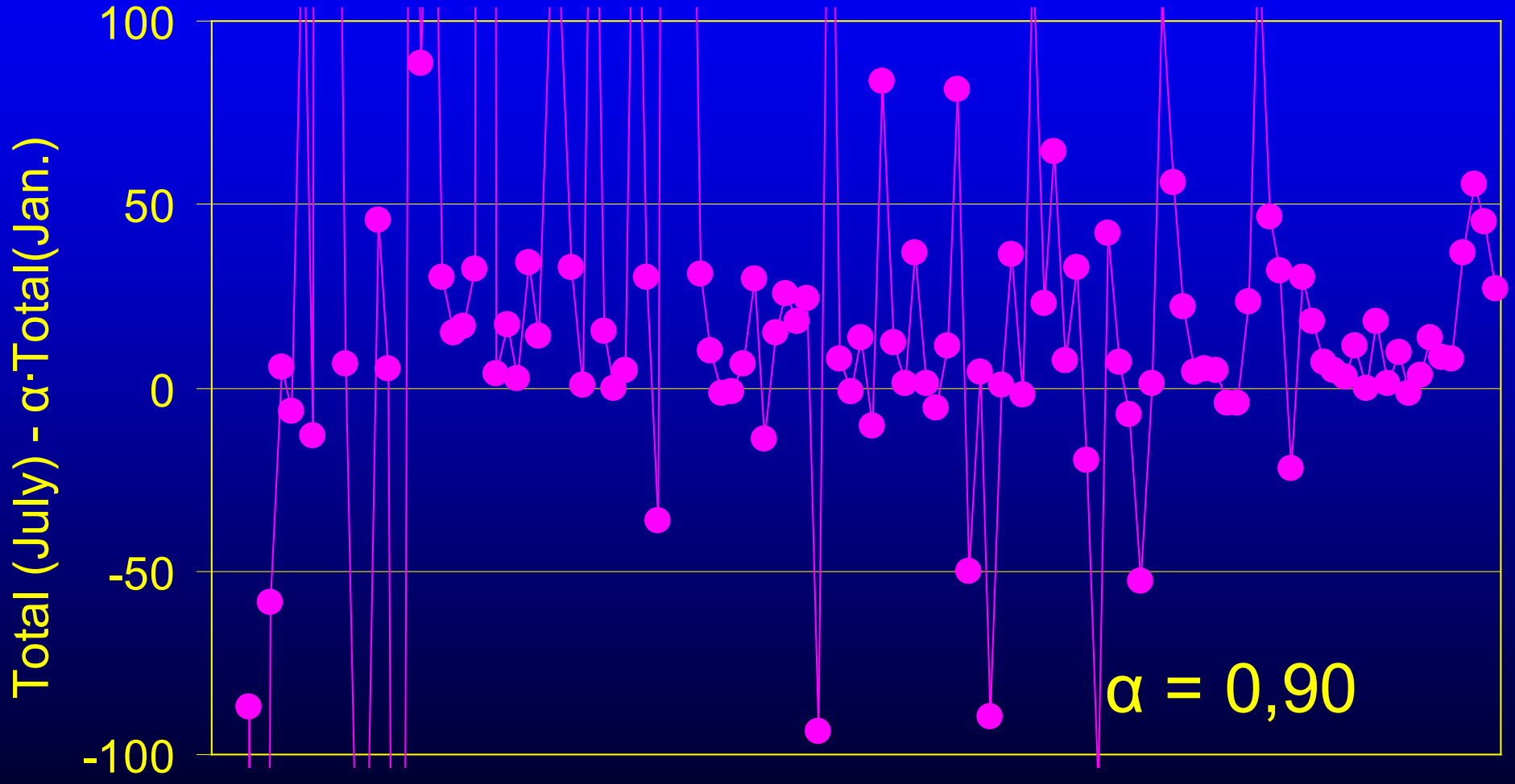


January 2004

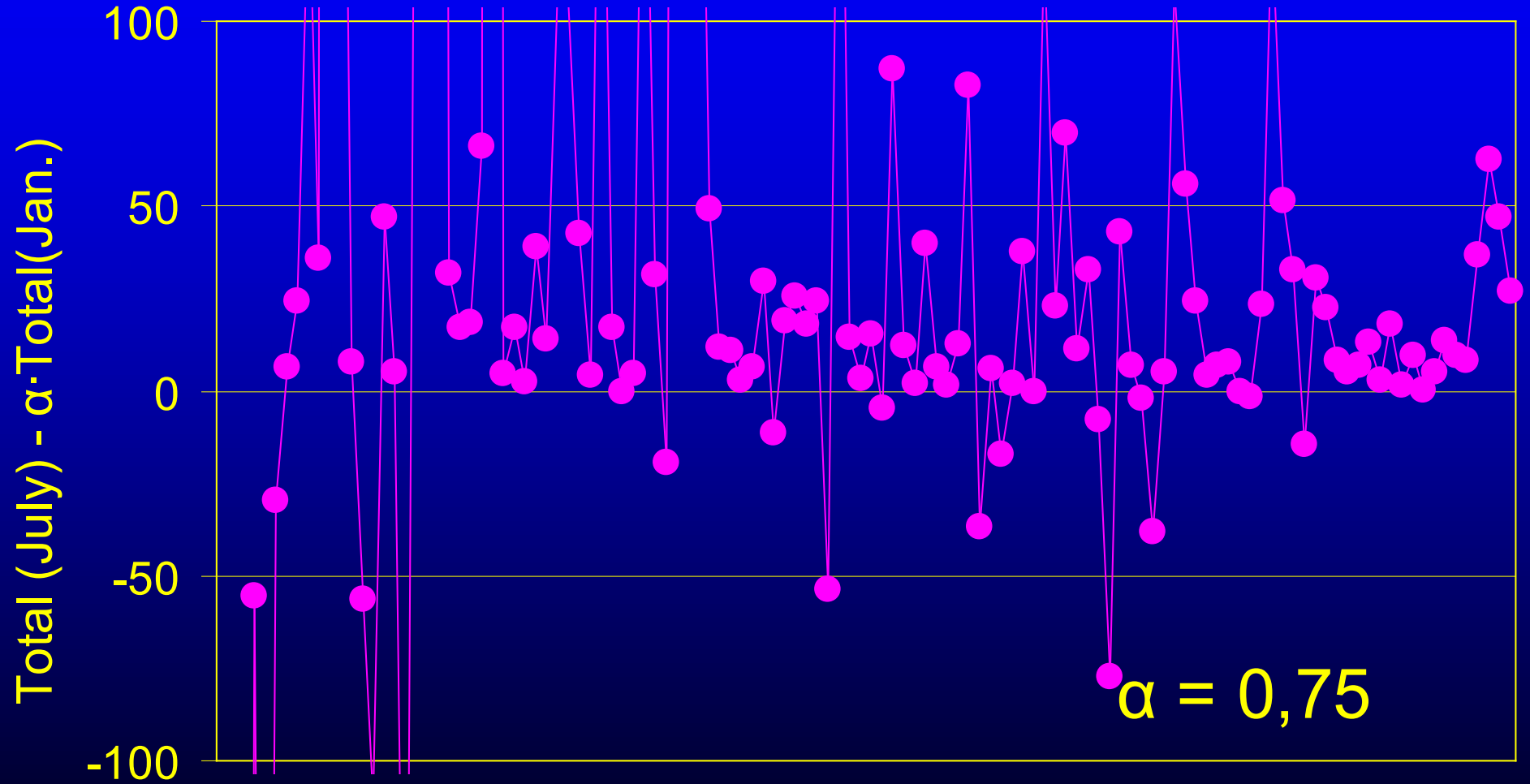
Estimation of the biogenic share of VOCs in July 2003

- July 2003: biogenic + anthropogenic VOCs
- January 2004: only anthropogenic VOCs
- Assumption: constant anthropogenic mix
- Mixing ratios not directly comparable (mixing height)
- Approach 1: Scaling of January-mix: biogenic(July) = total(July)-a·total(Jan.)

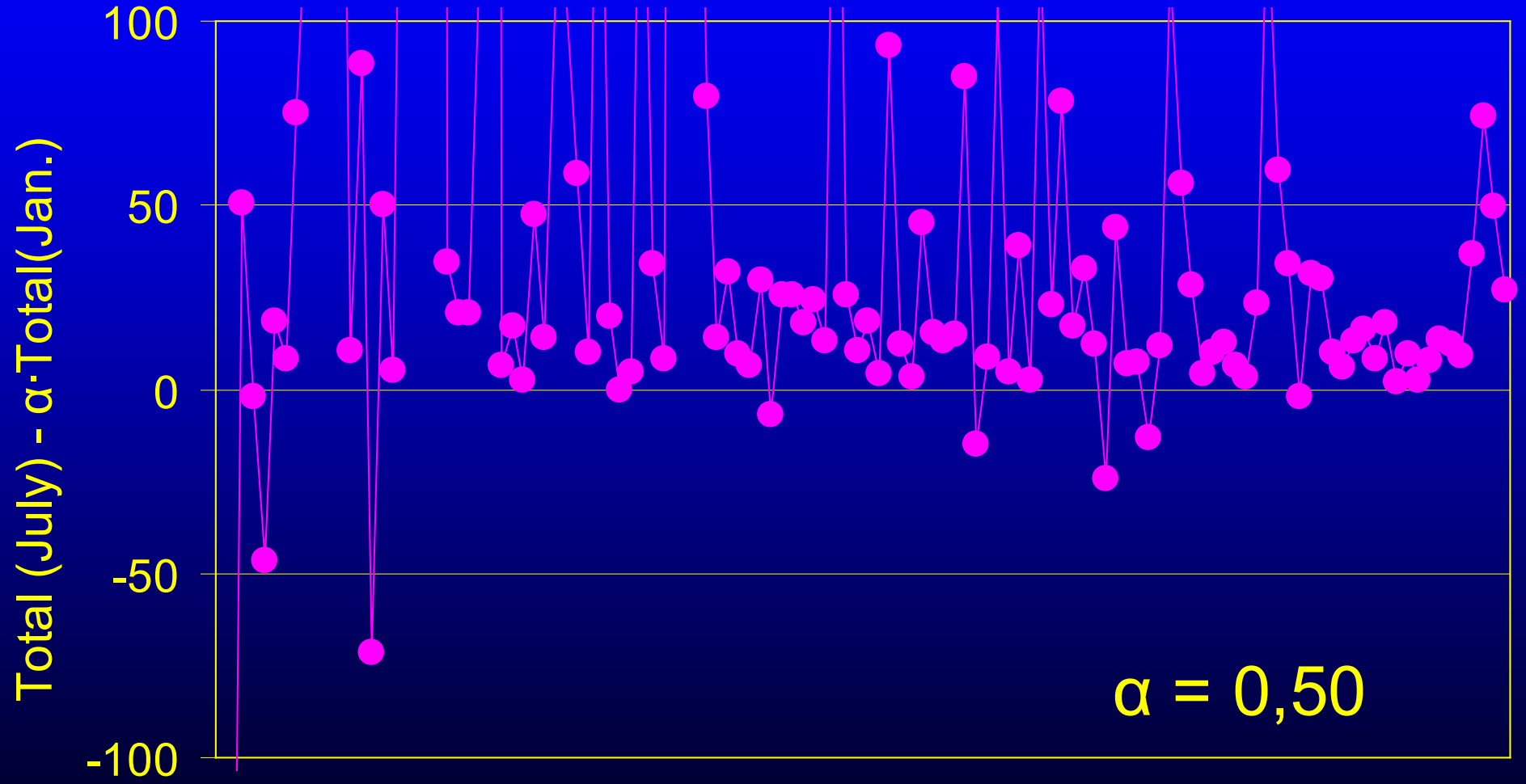
Estimation of biogenic share #1



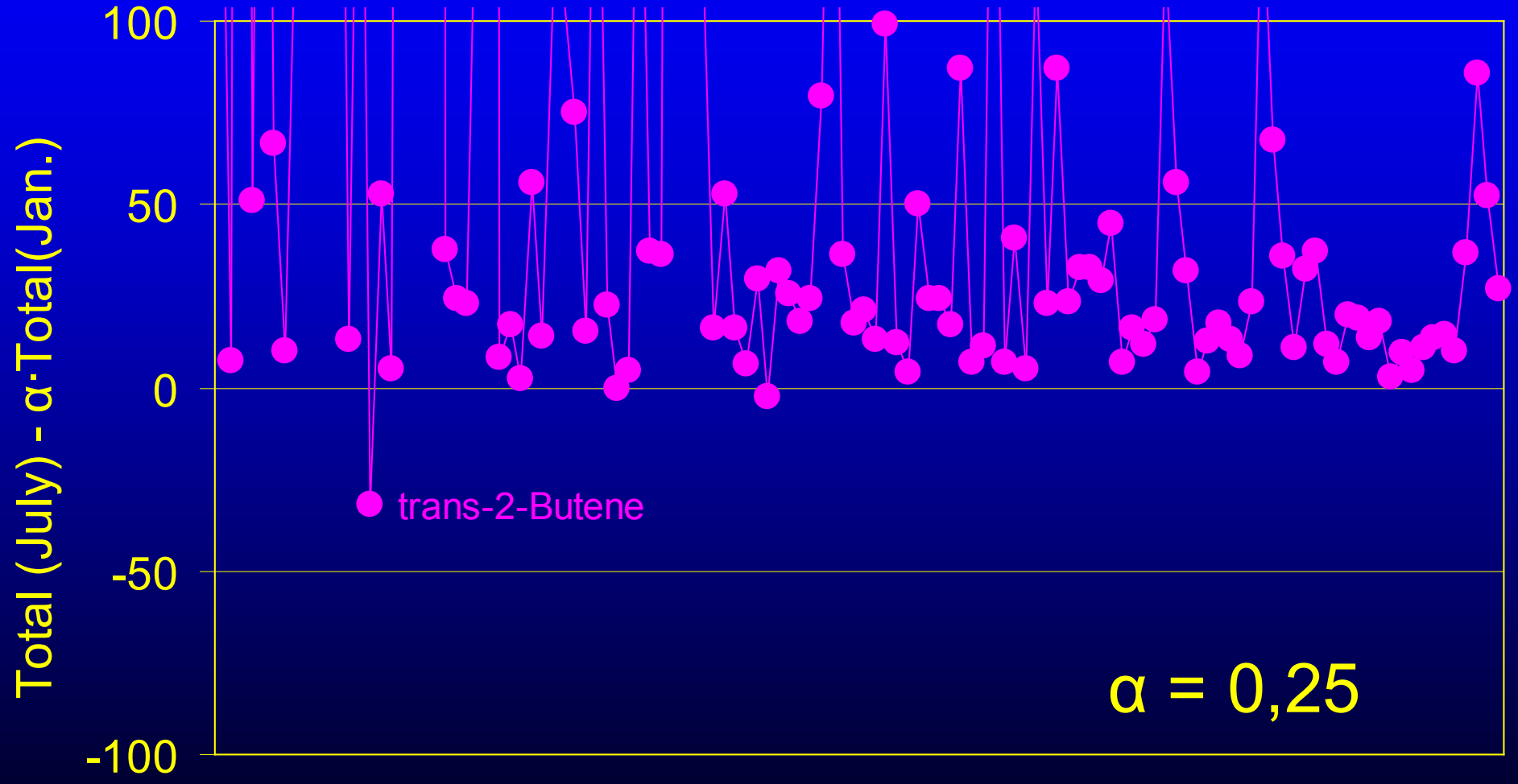
Estimation of biogenic share #1



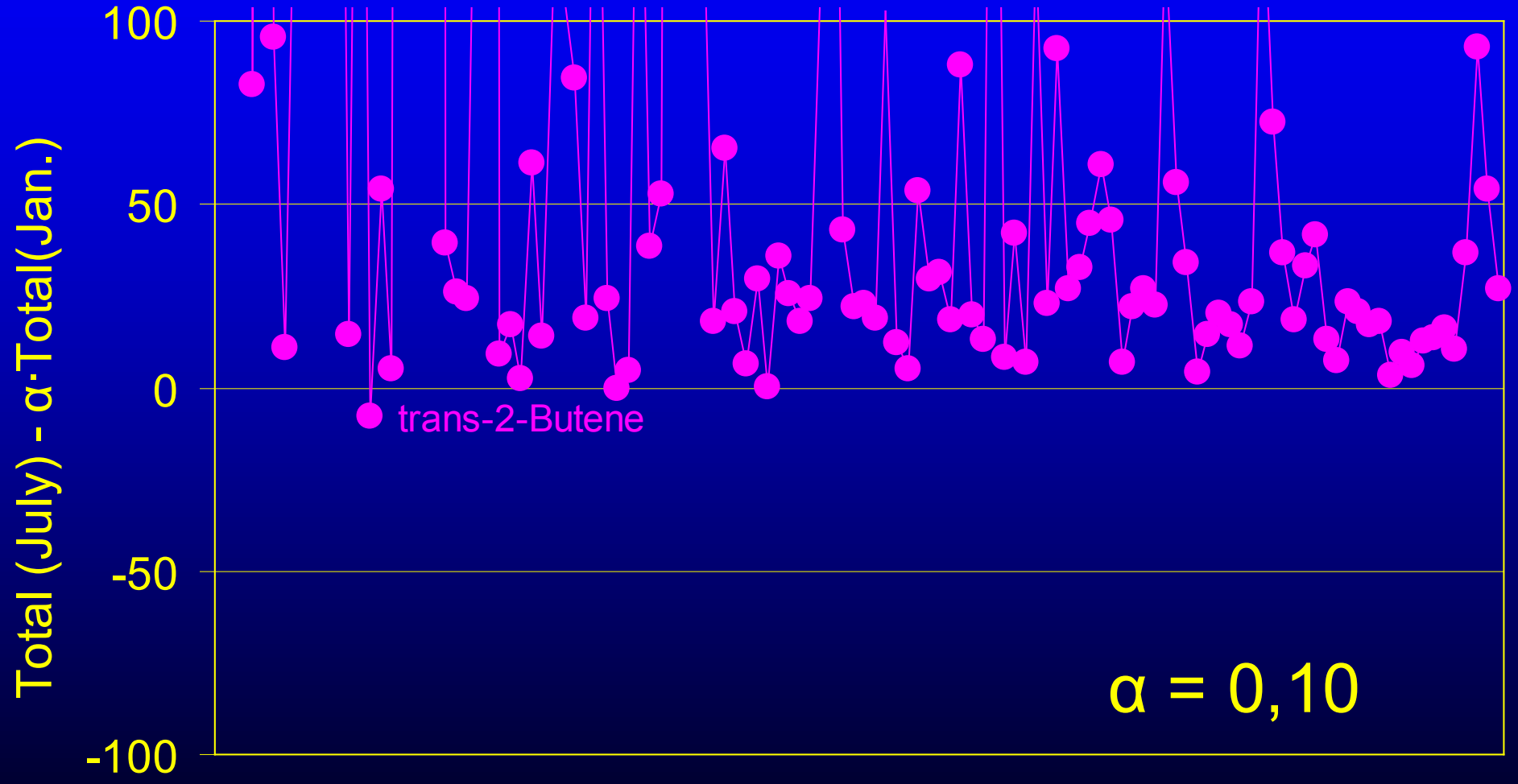
Estimation of biogenic share #1



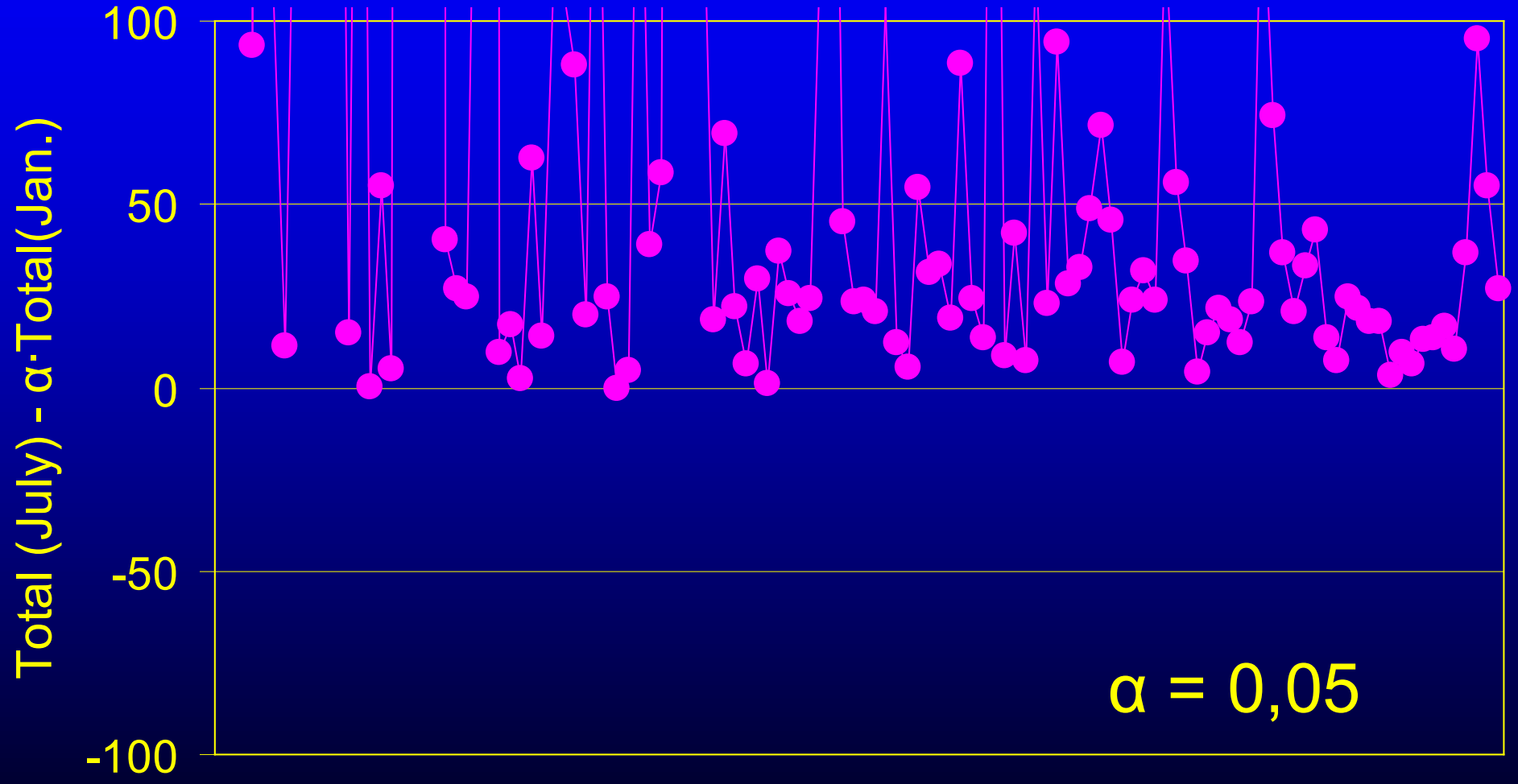
Estimation of biogenic share #1



Estimation of biogenic share #1



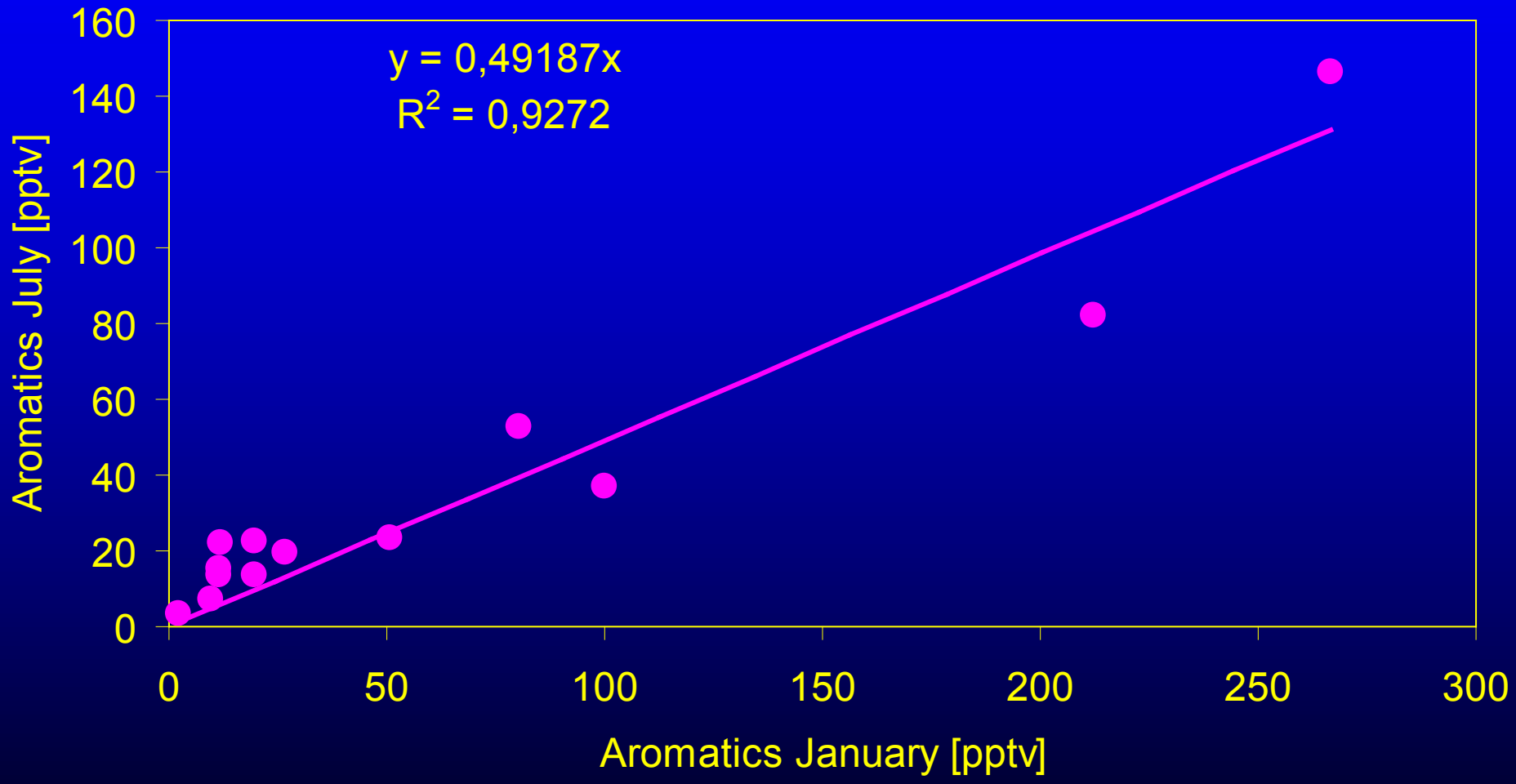
Estimation of biogenic share #1



Estimation of biogenic share #1

pptV		ppb·**kOH**·10E12		ppb·**kO_3**·10E18		ppb·**kNO_3**·10E15		µg/m^3·**POCP**	
biogenic	**20.099**	**biogenic**	**9,573**	**biogenic**	**1,729**	**biogenic**	**72,07**	**biogenic**	**2356**
in July	**78%**	**in July**	**96%**	**in July**	**97%**	**in July**	**97%**	**in July**	**81%**
Methanole	4583	Isoprene	6,939	Isoprene	0,961	Isoprene	48,214	Isoprene	865
Acetone	3511	Methyl vinyl ketc	0,210	cis-2-Butene	0,135	alpha-Pinene	4,512	Methyl vinyl ketc	100
Isoprene	2845	1-Hexene	0,188	1,3-Pentadiene	0,083	Cyclopentadiene	4,330	Methanole	79
Ethane	1017	1,3-Pentadiene	0,187	Methylcycloper	0,077	Limonene	3,968	Acetone	78
Ethanole	837	1-Butene / i-But	0,178	1-Butene / i-Bu	0,071	1,3-Pentadiene	2,967	1-Hexene	72
Methyl vinyl ke	696	Cyclopentadien	0,170	alpha-Pinene	0,063	Sabinene	2,332	1-Butene / i-But	69
Propane	373	Butyraldehyde	0,149	Limonene	0,059	beta-Pinene	1,626	o-Ethyltoluene	62
1-Butene / i-B	278	Methacrolein	0,127	1-Hexene	0,056	1-Butene / i-But	1,176	Butyraldehyde	61
Butyraldehyde	262	Methanole	0,106	Methyl vinyl ket	0,054	1,3-Hexadiene (	0,890	Ethanole	61
2-Methylbutan	261	Octene	0,080	2-Methyl-2-bute	0,033	2-Methyl-2-buter	0,788	Toluene	53

Estimation of biogenic share #2



Estimation of biogenic share #2

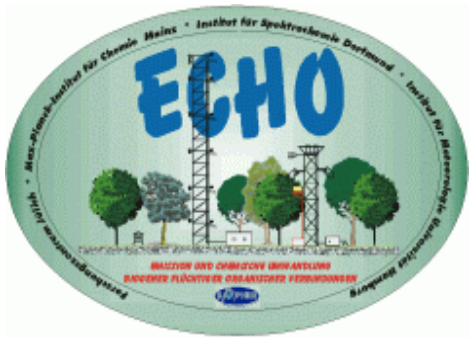
pptV		ppb·**kOH**·10E12		ppb·**kO_3**·10E18		ppb·**kNO_3**·10E15		µg/m^3·**POCP**	
biogenic	**14.858**	**biogenic**	**9,185**	**biogenic**	**1,680**	**biogenic**	**69,68**	**biogenic**	**2010**
in July	**58%**	**in July**	**92%**	**in July**	**94%**	**in July**	**94%**	**in July**	**69%**
Methanole	4069	Isoprene	6,930	Isoprene	0,960	Isoprene	48,158	Isoprene	864
Isoprene	2841	Methyl vinyl ketc	0,210	cis-2-Butene	0,128	alpha-Pinene	3,983	Methyl vinyl ketc	100
Acetone	2216	1,3-Pentadiene	0,187	1,3-Pentadiene	0,083	Cyclopentadiene	3,393	1-Hexene	71
Methyl vinyl ke	696	1-Hexene	0,187	Methylcycloper	0,077	Limonene	3,280	Methanole	70
Ethanole	301	1-Butene / i-But	0,172	1-Butene / i-Bu	0,068	1,3-Pentadiene	2,967	1-Butene / i-But	67
1-Butene / i-B	270	Butyraldehyde	0,149	alpha-Pinene	0,056	Sabinene	2,332	Butyraldehyde	61
Butyraldehyde	262	Cyclopentadien	0,134	1-Hexene	0,056	beta-Pinene	1,554	o-Ethyltoluene	59
3-Methyl-1-but	242	Methacrolein	0,127	Methyl vinyl ket	0,054	1-Butene / i-But	1,140	Acetone	49
1-Hexene	237	Methanole	0,094	Limonene	0,049	1,3-Hexadiene (	0,890	3-Methyl-1-buter	47
1-Butanole	222	Octene	0,078	2-Methyl-2-bute	0,033	2-Methyl-2-buter	0,788	Methacrolein	34

Summary Results July 2003

- Isoprene, ethane, ethanol, acetone and methanol yield highest concentrations 1-5 ppb
- Oxygenated compounds 49%
- Isoprene is responsible for 50-70% of reactivity and 1/3 of local ozone production
- Reactivity with NO_3 and ozone: >99% due to terpenes und alkenes
- OH-reactivity: 25% due to other compounds

Biogenic Share July 2003

	Approach 1	Approach 2
Mixing ratio	78%	58%
OH reactivity	96%	92%
Ozone reactivity	97%	94%
NO_3 reactivity	97%	94%
Ozone Production	81%	69%



I thank for your attention.

b.mittermaier@fz-juelich.de

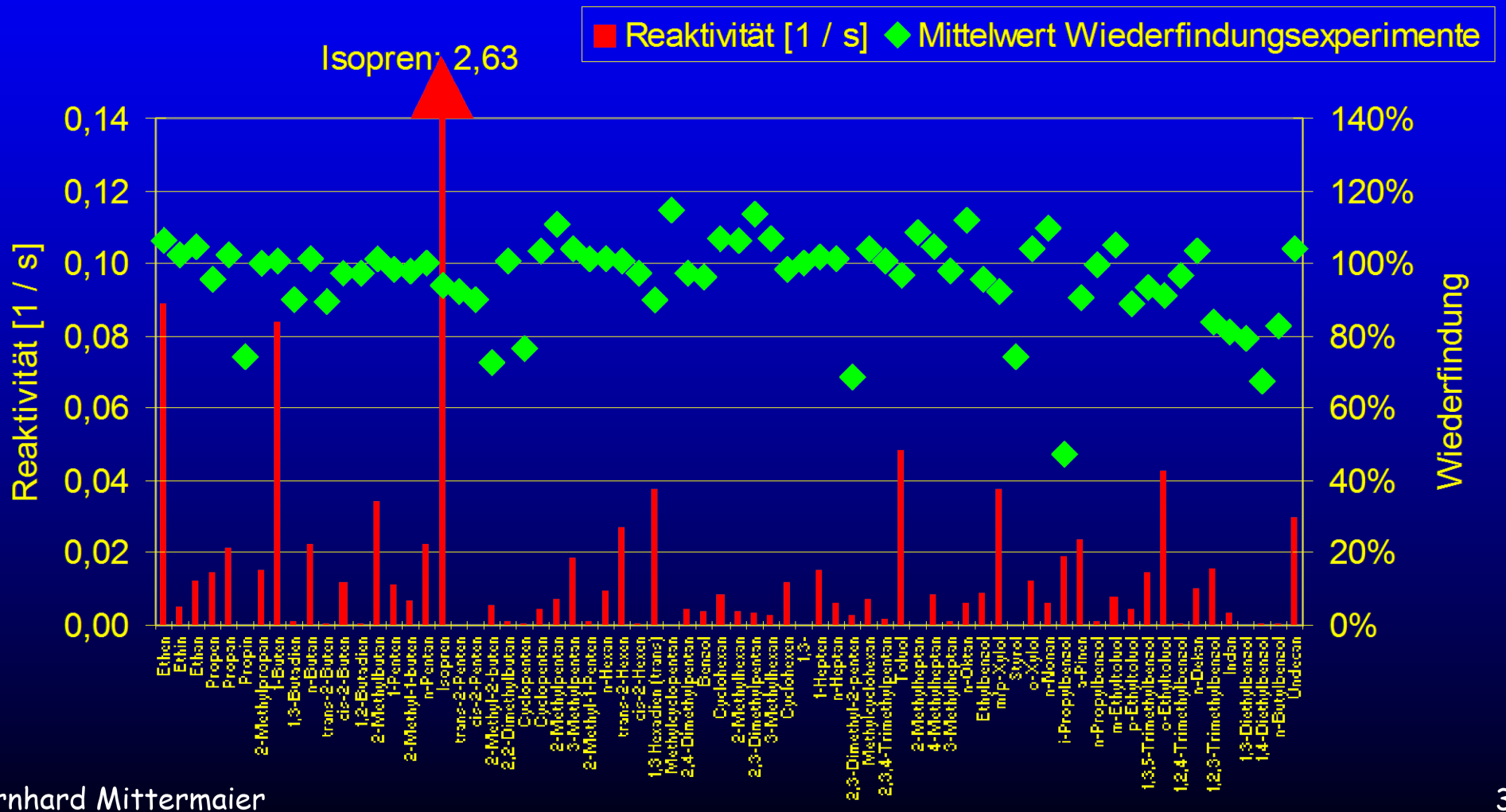
Calibration

- NMHC-standard 74 compounds
- VOC-standard 45 compounds
- Estimation of response via the concept of the "Effective Carbon Number" ECN

Recovery

- 100 ppb ozone in air
- 50 ppb ozone in canister
- approx. 40.000 ppb after pre-concentration
- precautions:
  - ozone-destruction during sampling
  - rinsing with hydrogen during re-mobilization of analytes
  - potassium iodide: considerable loss of HCs > C_8

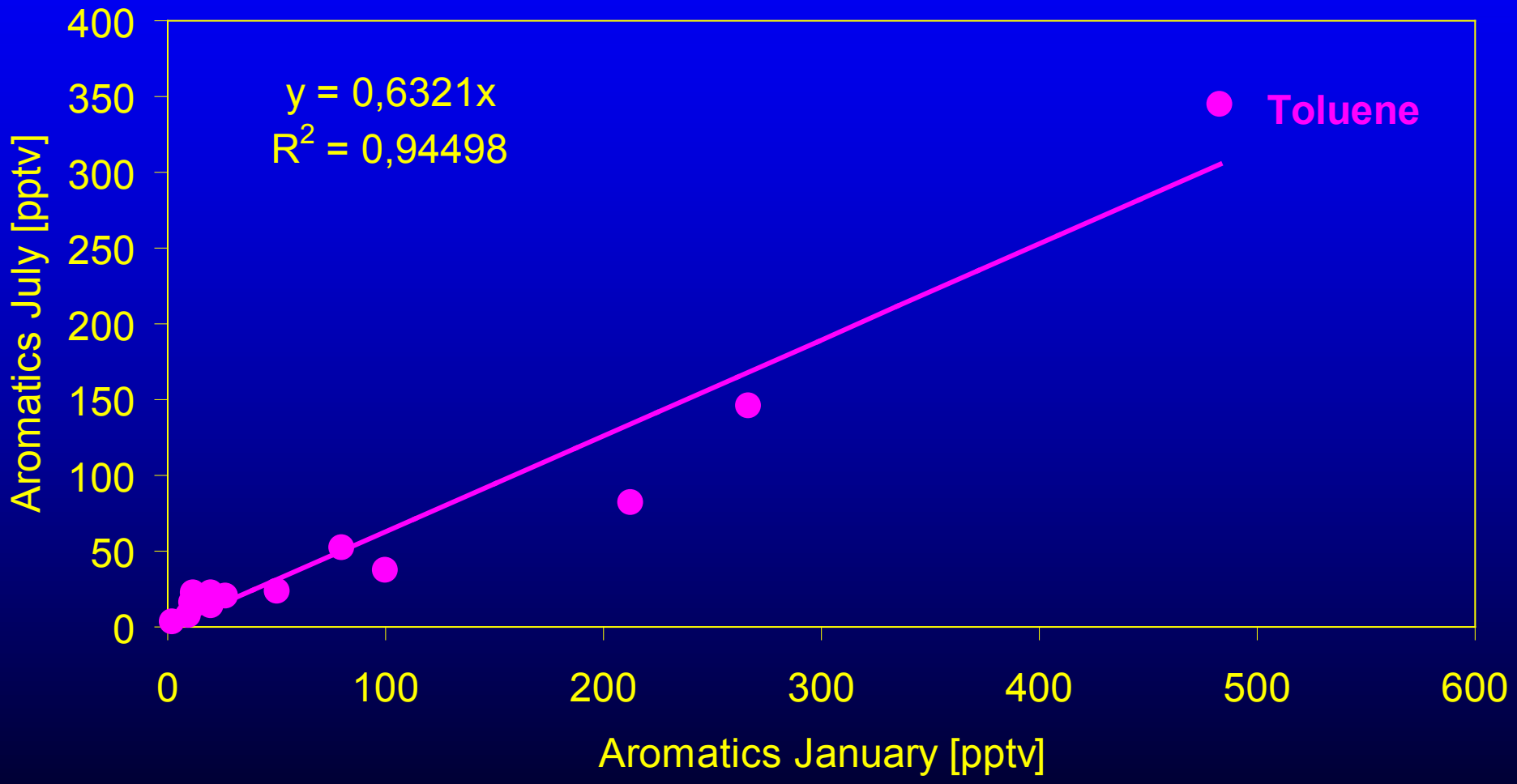
Recovery at 100 ppb Ozone



Analytes

- Alkanes C_2-C_{13}
- Alkenes C_2-C_9
- Aromatics C_6H_6- $C_6H_5C_4H_9$
- Monoterpenes
- Alcohols CH_3OH - C_4H_9OH
- Aldehydes CH_3CHO - $C_7H_{15}CHO$
- others (e.g. Acetates)

Estimation of biogenic share #2



Summary Results January 2004

- Acetylene, ethene, propane, methanol, ethanol, ethane and acetone 1 – 5 ppbV
- Oxygenated compounds 44%, alkanes 35%, alkenes 13%, terpenes <1%
- reactivity 60% lower than in July
- Numerous relatively high single reactivities